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(71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

(72) Inventors: **ZHANG, Joanna, Hong**; Unilever Home & Personal Care USA, 40 Merritt Boulevard, Trumbull, CT

06611 (US). **FARNIARZ, Joseph, Raymond**; Unilever Home & Personal Care USA, 40 Merritt Boulevard, Trumbull, CT 06611 (US). **CHENEY, Michael, Charles**; Unilever Home & Personal Care USA, 40 Merritt Boulevard, Trumbull, CT 06611 (US).

(74) Agents: **MULDER, Cornelis, Willem, Reinier** et al.; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

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(54) Title: SUNSCREEN COSMETIC COMPOSITIONS STORAGE STABILIZED WITH MALONATE SALTS

(57) Abstract: A cosmetic composition is provided which includes an organic sunscreen agent and at least one salt of a malonic acid. The malonate salt inhibits discoloration which may arise from the presence of the sunscreen agent. Of particular concern in forming color bodies is 4,4'-t-butyl-methoxydibenzoylmethane.

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SUNSCREEN COSMETIC COMPOSITIONS STORAGE STABILIZED WITH
MALONATE SALTS

5 The invention concerns sunscreen cosmetic compositions stabilized by malonate salts against decomposition during storage.

Sunscreen agents operate to shield human bodies from sun irradiation. Unfortunately, sunscreen agent upon occasion
10 will discolor the cosmetic formulations into which they are blended.

Organic acids have been disclosed as skin benefit agents in the cosmetic literature. For instance, malonic acid has been reported in U.S. Patent 5,641,495 (Jokura et al.) in
15 combination with ceramides or pseudoceramides as moisturization actives. No mention is found in the relevant literature that carboxylic acids or their salts stabilize organic sunscreen agents.

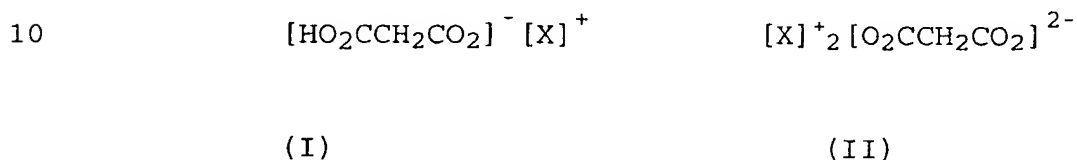
In a first aspect of the invention, there is provided a
20 cosmetic composition which includes:

- (i) from about 0.0001% to about 30% by weight of a salt of malonic acid;
- (ii) from about 0.05% to about 40% by weight of an organic sunscreen agent having a chromophoric
25 group active within the ultraviolet radiation range of 280 to 400 nm; and
- (iii) from about 1% to about 99.9% by weight of a cosmetically acceptable carrier.

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Now it has been found that malonate salts can inhibit discoloration of cosmetic compositions containing sunscreen agents.

A wide variety of malonate salts may be useful for this invention. Many types of counter cations to the malonate anions may be utilized in forming the salts. Malonate salts may either be the half or fully neutralized malonic acid or combinations thereof as represented by general formulas (I) and (II):



wherein X is a cationic counterion.

Suitable inorganic cationic counterions include those of alkali and alkaline earth metals. Representative examples
15 include the cations of lithium, sodium, potassium, magnesium, calcium, ammonium and combinations thereof.

Not only inorganic but also organic cations can be employed. Particularly useful are quaternized nitrogen cations having from 1 to 1,000, preferably from 1 to 20, and optimally from
20 3 to 12 carbon atoms. Illustrative are those cations derived from amines which include polyethyleneimine, triethanolamine, diethanolamine, propanolamine, monoethanolamine, methylamine, ethylamine, propylamine, isopropylamine, butylamine, isobutylamine, t-butylamine,
25 pentylamine, isopentylamine, hexylamine, cyclohexylamine,

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cyclopentylamine, norbornylamine, octylamine, ethylhexylamine, nonylamine, decylamine, pyrrolidone, amino acids (lysine, alamine, glutamine, histidine, glycine), 2-amino-2-methyl-1-propanol, dimethylethanolamine, 5 tris(hydroxymethyl)amino methane and combinations thereof. Most preferred are the cations derived from ammonia, dimethylethanolamine and tris(hydroxymethyl)amino methane. Preferred salts include ammonium malonate, diammonium malonate, dimethylethanolammonium malonate, 10 bis(dimethylethanolammonium)malonate, tris(hydroxymethyl)methane ammonium, malonate, and di[tris(hydroxymethyl)methane ammonium]malonate.

Amounts of the malonic acid salt may range from about 0.0001% to about 30%, preferably from about 0.1% to about 15%, more preferably from about 0.5% to about 10%, optimally 15 from about 1% to about 8% by weight of the cosmetic composition.

The present invention can utilize as the active ingredient salt I, salt II or mixtures of these salts. When mixtures 20 are present the molar ratio of mono-salt I to di-salt II may range from about 1000:1 to about 1:1000, preferably from about 10:1 to about 1:500, more preferably from about 2:1 to about 1:200, optimally from about 1:1 to about 1:20.

Sunscreen agents formulated into compositions of the present 25 invention are those organic substances having a chromophoric group active within the ultraviolet radiation range from 280 to 400 nm.

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Chromophoric functionalized organic sunscreen agents may be divided into the following categories (with specific examples), including:

- p-Aminobenzoic acid, its salts and its derivatives (ethyl, isobutyl, glyceryl esters; p-dimethylaminobenzoic acid); Anthranilates (o-aminobenzoates; methyl, menthyl, phenyl, benzyl, phenylethyl, linalyl, terpinyl, and cyclohexenyl esters); Salicylates (octyl, amyl, phenyl, benzyl, menthyl, glyceryl, and dipropyleneglycol esters); Cinnamic acid derivatives (menthyl and benzyl esters, alpha-phenyl cinnamionitrile; butyl cinnamoyl pyruvate); Dihydroxycinnamic acid derivatives (umbelliferone, methylumbelliferone, methylaceto-umbelliferone); Trihydroxycinnamic acid derivatives (esculetin, methylesculetin, daphnetin, and the glucosides, esculin and daphnin); Hydrocarbons (diphenylbutadiene, stilbene); Dibenzalacetone and benzalacetophenone; Naphtholsulfonates (sodium salts of 2-naphthol-3,6-disulfonic and of 2-naphthol-6,8-disulfonic acids); Dihydroxy-naphthoic acid and its salts; o- and p-Hydroxydiphenyldisulfonates; Coumarin derivatives (7-hydroxy, 7-methyl, 3-phenyl); Diazoles (2-acetyl-3-bromoindazole, phenyl benzoxazole, methyl naphthoxazole, various aryl benzothiazoles); Quinine salts (bisulfate, sulfate, chloride, oleate, and tannate); Quinoline derivatives (8-hydroxyquinoline salts, 2-phenylquinoline); Hydroxy-or-methoxy-substituted benzophenones; Uric and vilouric acids; Tannic acid and its derivatives; Hydroquinone; Benzophenones (Oxybenzone, Sulisobenzene, Dioxybenzone, Benzoresorcinol, 2,2',4,4'-Tetrahydroxybenzophenone, 2,2'-Dihydroxy-4,4'-dimethoxybenzophenone, Octabenzene, 4-

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isopropylidibenzoylmethane, Butylmethoxydibenzoylmethane, Etocrylene, and 4-isopropyl-dibenzoylmethane).

Particularly important are: 2-ethylhexyl p-methoxycinnamate, 4,4'-t-butyl methoxydibenzoylmethane, 2-hydroxy-4-
5 methoxybenzophenone, octyldimethyl p-aminobenzoic acid, digalloyltriolate, 2,2-dihydroxy-4-methoxybenzophenone, ethyl 4-[bis(hydroxypropyl)] aminobenzoate, 2-ethylhexyl-2-cyano-3,3-diphenylacrylate, 2-ethylhexylsalicylate, glycerol p-aminobenzoate, 3,3,5-trimethylcyclohexylsalicylate,
10 methylantranilate, p-dimethylaminobenzoic acid or aminobenzoate, 2-ethylhexyl p-dimethylaminobenzoate, 2-phenylbenzimidazole-5-sulfonic acid, 2-(p-dimethylaminophenyl-5-sulfoniobenzoxazoic acid and mixtures thereof.

15

Suitable commercially available organic sunscreen agents are those identified under the following table.

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TABLE I

CTFA NAME	TRADE NAME	SUPPLIER
Benzophenone-3	UVINUL M-40	BASF Chemical Co.
Benzophenone-4	UVINUL MS-40	BASF Chemical Co.
Benzophenone-8	SPECTRA-SORB UV-24	American Cyanamid
DEA-Methoxycinnamate	BERNEL HYDRO	Bernel Chemical
Ethyl dihydroxypropyl-PABA	AMERSCREEN P	Amerchol Corp.
Glyceryl PABA	NIPA G.M.P.A.	Nipa Labs.
Homosalate	KEMESTER HMS	Humko Chemical
Menthyl anthranilate	SUNAROME UVA	Felton Worldwide
Octocrylene	UVINUL N-539	BASF Chemical Co.
Octyl dimethyl PABA	AMERSCOL	Amerchol Corp.
Octyl methoxycinnamate	PARSOL MCX	Bernel Chemical
PABA	PABA	National Starch
2-Phenylbenzimidazole-5-sulphonic acid	EUSOLEX 6300	EM Industries
TEA salicylate	SUNAROME W	Felton Worldwide
2-(4-Methylbenzildene)-camphor	EUSOLEX 6300	EM Industries
Benzophenone-1	UVINUL 400	BASF Chemical Co.
Benzophenone-2	UVINUL D-50	BASF Chemical Co.
Benzophenone-6	UVINUL D-49	BASF Chemical Co.
Benzophenone-12	UVINUL 408	BASF Chemical Co.
4-Isopropyl dibenzoyl methane	EUSOLEX 8020	EM Industries
Butyl Methoxy dibenzoyl methane	PARSOL 1789	Givaudan Corp.
Etocrylene	UVINUL N-35	BASF Chemical Co.

Particularly discoloration promoting materials are UVA type
 5 of sunscreens, the most evident of which is 4, 4'-t-butylmethoxydibenzoylmethane available commercially as
 Parsol 1789®.

Amounts of the aforementioned sunscreen agents will
 generally range from about 0.05% to about 40%, preferably
 10 from about 1% to about 30%, more preferably from about 2% to
 about 15%, optimally from about 4% to about 10% by weight.

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Compositions of this invention will also include a cosmetically acceptable carrier. Amounts of the carrier may range from 1% to 99.9%, preferably from about 70% to about 95%, optimally from about 80% to about 90%. Among the
5 useful carriers are water, emollients, fatty acids, fatty alcohols, humectants, thickeners and combinations thereof. The carrier may be aqueous, anhydrous or an emulsion. Preferably the compositions are aqueous, especially water and oil emulsions of the W/O or O/W variety. Water when
10 present may be in amounts ranging from about 5% to about 95%, preferably from about 20% to about 70%, optimally from about 35% to about 60% by weight.

Emollient materials may serve as cosmetically acceptable carriers. These may be in the form of silicone oils,
15 synthetic esters and hydrocarbons. Suitable amounts of the emollients may range anywhere from about 0.1% to about 95%, preferably between about 1% and about 50% by weight.

Silicone oils may be divided into the volatile and nonvolatile variety. The term "volatile" as used herein
20 refers to those materials which have a measurable vapor pressure at ambient temperature. Volatile silicone oils are preferably chosen from cyclic (cyclomethicone) or linear polydimethylsiloxanes containing from 3 to 9, preferably from 4 to 5, silicon atoms.

25 Non-volatile silicone oils useful as an emollient material include polyalkyl siloxanes, polyalkylaryl siloxanes and polyether siloxane copolymers. The essentially non-volatile polyalkyl siloxanes useful herein include, for example,

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polydimethyl siloxanes with viscosities of from about 5×10^{-6} to $0.1 \text{ m}^2/\text{s}$ at 25°C . Among the preferred non-volatile emollients useful in the present compositions are the polydimethyl siloxanes having viscosities from about 1×10^{-5} to about $4 \times 10^{-4} \text{ m}^2/\text{s}$ at 25°C .

Another class of nonvolatile silicones are emulsifying and non-emulsifying silicone elastomers. Representative of this category is Dimethicone/Vinyl Dimethicone Crosspolymer available as Dow Corning 9040, General Electric SFE 839, and Shin-Etsu KSG-18. Silicone waxes such as Silwax WS-L (Dimethicone Copolyol Laurate) may also be useful.

Among the suitable ester emollients are:

- (1) Alkenyl or alkyl esters of fatty acids having 10 to 20 carbon atoms. Examples thereof include isoarachidyl neopentanoate, isononyl isononanoate, oleyl myristate, oleyl stearate, and oleyl oleate.
- (2) Ether-esters such as fatty acid esters of ethoxylated fatty alcohols.
- (3) Polyhydric alcohol esters. Ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol (200-6000) mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol 2000 monooleate, polypropylene glycol 2000 monostearate, ethoxylated propylene glycol

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monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol poly-fatty esters, ethoxylated glyceryl mono-stearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, 5 polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters are satisfactory polyhydric alcohol esters. Particularly useful are pentaerythritol, trimethylolpropane and neopentyl 10 glycol esters of C₁-C₃₀ alcohols.

(4) Wax esters such as beeswax, spermaceti wax and tribehenin wax.

(5) Sterols esters, of which cholesterol fatty acid esters are examples thereof.

15 (6) Sugar ester of fatty acids such as sucrose polybehenate and sucrose polycottonseedate.

Hydrocarbons which are suitable cosmetically acceptable carriers include petrolatum, mineral oil, C₁₁-C₁₃ isoparaffins, polyalphaolefins, and especially 20 isohexadecane, available commercially as Permethyl 101A from Presperse Inc.

Fatty acids having from 10 to 30 carbon atoms may also be suitable as cosmetically acceptable carriers. Illustrative of this category are pelargonic, lauric, myristic, palmitic, 25 stearic, isostearic, hydroxystearic, oleic, linoleic, ricinoleic, arachidic, behenic and erucic acids.

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Fatty alcohols having from 10 to 30 carbon atoms are another useful category of cosmetically acceptable carrier.

Illustrative of this category are stearyl alcohol, lauryl alcohol, myristyl alcohol and cetyl alcohol.

- 5 Humectants of the polyhydric alcohol-type can be employed as cosmetically acceptable carriers. Typical polyhydric alcohols include glycerol, polyalkylene glycols and more preferably alkylene polyols and their derivatives, including propylene glycol, dipropylene glycol, polypropylene glycol, 10 polyethylene glycol and derivatives thereof, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1,3-butylene glycol, isoprene glycol, 1,2,6-hexanetriol, ethoxylated glycerol, propoxylated glycerol and mixtures thereof. The amount of humectant may range anywhere from 0.5% to 50%, 15 preferably between 1% and 15% by weight of the composition.

- Thickeners can be utilized as part of the cosmetically acceptable carrier of compositions according to the present invention. Typical thickeners include crosslinked acrylates (e.g. Carbopol 982®), hydrophobically-modified acrylates 20 (e.g. Carbopol 1382®), cellulosic derivatives and natural gums. Among useful cellulosic derivatives are sodium carboxymethylcellulose, hydroxypropyl methocellulose, hydroxypropyl cellulose, hydroxyethyl cellulose, ethyl cellulose and hydroxymethyl cellulose. Natural gums 25 suitable for the present invention include guar, xanthan, sclerotium, carrageenan, pectin and combinations of these gums. Inorganics may also be utilized as thickeners, particularly clays such as bentonites and hectorites, fumed

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silicas, and silicates such as magnesium aluminum silicate (Veegum®). Amounts of the thickener may range from 0.0001% to 10%, usually from 0.001% to 1%, optimally from 0.01% to 0.5% by weight.

- 5 Cosmetic compositions of the present invention may be in any form. These forms may include lotions, creams, roll-on formulations, sticks, mousses, aerosol and non-aerosol sprays and fabric (e.g. nonwoven textile)-applied formulations.
- 10 Surfactants may also be present in cosmetic compositions of the present invention. Total concentration of the surfactant when present may range from about 0.1% to about 40%, preferably from about 1% to about 20%, optimally from about 1% to about 5% by weight of the composition. The
- 15 surfactant may be selected from the group consisting of anionic, nonionic, cationic and amphoteric actives. Particularly preferred nonionic surfactants are those with a C₁₀-C₂₀ fatty alcohol or acid hydrophobe condensed with from 2 to 100 moles of ethylene oxide or propylene oxide per mole
- 20 of hydrophobe; C₂-C₁₀ alkyl phenols condensed with from 2 to 20 moles of alkylene oxide; mono- and di-fatty acid esters of ethylene glycol; fatty acid monoglyceride; sorbitan, mono- and di- C₈-C₂₀ fatty acids; and polyoxyethylene sorbitan as well as combinations thereof. Alkyl
- 25 polyglycosides and saccharide fatty amides (e.g. methyl gluconamides) are also suitable nonionic surfactants.

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Preferred anionic surfactants include soap, alkyl ether sulfates and sulfonates, alkyl sulfates and sulfonates, alkylbenzene sulfonates, alkyl and dialkyl sulfosuccinates, C₈-C₂₀ acyl isethionate, C₈-C₂₀ alkyl ether phosphates, C₈-C₂₀ sarcosinates and combinations thereof.

Preservatives can desirably be incorporated into the cosmetic compositions of this invention to protect against the growth of potentially harmful microorganisms. Suitable traditional preservatives for compositions of this invention are alkyl esters of para-hydroxybenzoic acid. Other preservatives which have more recently come into use include hydantoin derivatives, propionate salts, and a variety of quaternary ammonium compounds. Cosmetic chemists are familiar with appropriate preservatives and routinely choose them to satisfy the preservative challenge test and to provide product stability. Particularly preferred preservatives are phenoxyethanol, methyl paraben, propyl paraben, imidazolidinyl urea, sodium dehydroacetate and benzyl alcohol. The preservatives should be selected having regard for the use of the composition and possible incompatibilities between the preservatives and other ingredients in the emulsion. Preservatives are preferably employed in amounts ranging from 0.01% to 2% by weight of the composition.

Compositions of the present invention may include vitamins. Illustrative vitamins are Vitamin A (retinol), Vitamin B₂, Vitamin B₆, Vitamin C, Vitamin E and Biotin. Derivatives of the vitamins may also be employed. For instance, Vitamin C

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derivatives include ascorbyl tetraispalmitate, magnesium ascorbyl phosphate and ascorbyl glycoside. Derivatives of Vitamin E include tocopheryl acetate, tocopheryl palmitate and tocopheryl linoleate. DL-panthenol and derivatives may
5 also be employed. Total amount of vitamins when present in compositions according to the present invention may range from 0.001% to 10%, preferably from 0.01% to 1%, optimally from 0.1% to 0.5% by weight.

Another type of useful substance can be that of an enzyme
10 such as oxidases, proteases, lipases and combinations. Particularly preferred is superoxide dismutase, commercially available as Biocell SOD from the Brooks Company, USA.

Skin lightening compounds may be included in the compositions of the invention. Illustrative substances are
15 placental extract, lactic acid, niacinamide, arbutin, kojic acid, ferulic acid, resorcinol and derivatives including 4-substituted resorcinols and combinations thereof. Amounts of these agents may range from about 0.1% to about 10%, preferably from about 0.5% to about 2% by weight of the
20 composition.

Desquamation promoters may be present. Illustrative are the alpha-hydroxycarboxylic acids and beta-hydroxycarboxylic acids. The term "acid" is meant to include not only the free acid but also salts and C₁-C₃₀ alkyl or aryl esters
25 thereof and lactones generated from removal of water to form cyclic or linear lactone structures. Representative acids are glycolic, lactic and malic acids. Salicylic acid is representative of the beta-hydroxycarboxylic acids. Amounts

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of these materials when present may range from about 0.1% to about 15% by weight of the composition.

A variety of herbal extracts may optionally be included in compositions of this invention. Illustrative are green tea, chamomile, licorice and extract combinations thereof. The
5 extracts may either be water soluble or water-insoluble carried in a solvent which respectively is hydrophilic or hydrophobic. Water and ethanol are the preferred extract solvents.

- 10 Also included may be such materials as lipoic acid, retinoytrimethylsilane (available from Clariant Corp. under the Silcare 1M-75 trademark), dehydroepiandrosterone (DHEA) and combinations thereof. Ceramides (including Ceramide 1, Ceramide 3, Ceramide 3B and Ceramide 6) as well as
15 pseudoceramides may also be utilized but in many compositions of the present invention these ceramides and pseudoceramides may also be excluded. Amounts of these materials may range from about 0.000001% to about 10%, preferably from about 0.0001% to about 1% by weight.
- 20 Colorants, fragrances, opacifiers and abrasives may also be included in compositions of the present invention. Each of these substances may range from about 0.05% to about 5%, preferably between 0.1% and 3% by weight.

The term "comprising" is meant not to be limiting to any
25 subsequently stated elements but rather to encompass non-specified elements of major or minor functional importance. In other words the listed steps, elements or options need

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not be exhaustive. Whenever the words "including" or "having" are used, these terms are meant to be equivalent to "comprising" as defined above.

Examples

- 5 Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts of material ought to be understood as modified by the word "about".

- 10 The following examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise illustrated.

Example 1

- 15 A typical cosmetic cream according to the present invention is outlined under Table II.

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TABLE II

INGREDIENT	WEIGHT %
PHASE A	
Water	Balance
Disodium EDTA	0.05
Methyl Paraben	0.15
Magnesium Aluminum Silicate	0.60
Triethanolamine	1.20
PHASE B	
Xanthan Gum	0.20
Natrosol® 250HHR (ethyl cellulose)	0.50
Butylene Glycol	3.00
Glycerin	2.00
PHASE C	
Sodium Stearoyl Lactylate	0.10
Glycerol Monostearate	1.50
Stearyl Alcohol	1.50
Isostearyl Palmitate	3.00
Silicone Fluid	1.00
Cholesterol	0.25
Sorbitan Stearate	1.00
Butylated Hydroxy Toluene	0.05
Vitamin E Acetate	0.01
PEG-100 Stearate	2.00
Stearic Acid	3.00
Propyl Paraben	0.10
Parsol MCX®	2.00
Parsol 1789®	2.00
Caprylic/Capric Triglyceride	0.50
Hydroxycaprylic Acid	0.01
C12-15 Alkyl Octanoate	3.00
PHASE D	
Diammonium Malonate	3.00
PHASE E	
Vitamin A Palmitate	0.10
Bisabolol	0.01
Vitamin A Acetate	0.01
Fragrance	0.03
Retinol 50C	0.02

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Example 2

A water-in-oil topical liquid make-up foundation utilizing the malonate salts for color stabilization of the present invention is described in Table III below.

TABLE III

INGREDIENT	WEIGHT %
PHASE A	
Cyclomethicone	9.25
Cetyl Octanoate	2.00
Dimethicone Copolyol	20.00
Parsol 1789®	5.00
PHASE B	
Talc	3.38
Pigment (Iron Oxides)	10.51
Spheron L-1500 (Silica)	0.50
PHASE C	
Synthetic Wax Durachem 0602	0.10
Arachidyl Behenate	0.30
PHASE D	
Cyclomethicone	1.00
Trihydroxystearin	0.30
PHASE E	
Laureth-7	0.50
Propyl Paraben	0.25
PHASE F	
Fragrance	0.05
PHASE G	
Water	balance
Ammonium Malonate	3.00
Methyl Paraben	0.12
Propylene Glycol	8.00
Niacinamide	4.00
Glycerin	3.00
Sodium Chloride	2.00
Sodium Dehydroacetate	0.30

Example 3

Illustrated herein is a skin cream incorporating for color stabilization the malonate salts of the present invention.

5

TABLE IV

INGREDIENT	WEIGHT %
Glycerin	6.93
Niacinamide	5.00
Dimethylethanolammonium Malonate	5.00
Parsol 1789®	5.00
Permethyl 101A ¹	3.00
Sepigel 305 ²	2.50
Q2-1403 ³	2.00
Isopropyl Isostearate	1.33
Arlatone 2121 ⁴	1.00
Cetyl Alcohol CO-1695	0.72
SEFA Cottonate ⁵	0.67
Tocopherol Acetate	0.50
Panthenol	0.50
Stearyl Alcohol	0.48
Titanium Dioxide	0.40
Disodium EDTA	0.10
Glydant Plus ⁶	0.10
PEG-100 Stearate	0.10
Stearic Acid	0.10
Purified Water	Balance

¹ Isohexadecane, Presperse Inc., South Plainfield, NJ

² Polyacrylamide (and) C13-14 Isoparaffin (and) Laureth-7,
10 Seppic Corporation, Fairfield, NJ

³ Dimethicone (and) dimethiconol, Dow Corning Corp. Midland, MI

⁴ Sorbitan Monostearate and Sucrococoate, ICI Americas Inc.,
Wilmington, DE

⁵ Sucrose ester of fatty acid

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⁶ DMDM Hydantoin (and) Iodopropynyl Butylcarbamate, Lonza Inc., Fairlawn, NJ

5 Example 4

Illustrative of a powdered cosmetic composition according to the present invention is the formula of Table V.

10

TABLE V

INGREDIENT	WEIGHT %
Polysilicone-11	22.5
Cyclomethicone	56
Petrolatum	11
Parsol 1789®	3
Tris(hydroxymethyl)methaneammonium Malonate	7
Dimethicone Copolyol	0.5

Example 5

15

A relatively anhydrous composition according to the present invention is reported in Table VI.

TABLE VI

INGREDIENT	WEIGHT %
Cyclomethicone	74.65
Dimethicone	9.60
Parsol 1789®	6.00
Squalane	6.00
Isostearic Acid	1.90
Borage Seed Oil	0.90
Ammonium Malonate (50% in water)	0.50
Retinyl Palmitate	0.25
Ceramide 6	0.10
Tocopherol	0.10

20

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Example 6

An aerosol packaged foaming cleanser suitable for the present invention is outlined in Table VII.

5

TABLE VII

INGREDIENT	WEIGHT %
Sunflower Seed Oil	20.00
Parsol 1789®	6.00
Parsol MCX®	4.00
Maleated Soybean Oil	5.00
Silicone Urethane	1.00
Polyglycero-4 Oleate	1.00
Sodium C14-16 Olefin Sulfonate	15.00
Sodium Lauryl Ether Sulphate (25% active)	15.00
Cocoamidopropylbetaine	15.00
DC 1784® (Silicone Emulsion 50%)	5.00
Polyquaternium-11	1.00
Bis(dimethylethanolammonium) Malonate	1.00
Water	Balance

- 10 An aerosol is prepared using 92% by weight of the concentrate in Table VI and 8% propellant, the latter being a combination of dimethylether, isobutane and propane.

Example 7

- 15 An adhesive cosmetic patch may also be formulated according to the present invention. An adhesive hydrogel is prepared by mixing 30 grams of 2-acrylamido-2-methylpropane sulphonic acid monomer in 20 grams distilled water and 5 grams of a 1% aqueous solution of methylene-bis-acrylamide. The solution
- 20 is then activated with 0.4% magnesium persulphate catalyst. Shortly after mixing the catalyst with the hydrogel

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solution, 0.1 grams ammonium malonate and 0.05 grams Parsol 1789® in 5 ml water/ethanol is added. The resultant solution is coated onto a 50/50 blend of polypropylene and hydrophilic polyester and allowed to solidify. The
 5 resulting deposited hydrogel is warmed for 24 hours at 40°C in a hot air oven. Final water content of the hydrogel is 50%. A polystyrene backing layer is laid over the adhesive hydrogel. Discoloration is prevented by the malonate salt.

10 Example 8

A disposable, single use personal towelette product is described according to the present invention. A 70/30 polyester/rayon non-woven towelette is prepared with a weight
 15 of 1.8 grams and dimensions of 15cm by 20cm. Onto this towelette is impregnated a composition as outlined in Table VIII below.

TABLE VIII

INGREDIENT	WEIGHT %
Magnesium Malonate	7.50
Glycerin	2.00
Hexylene Glycol	2.00
Parsol 1789®	1.00
Disodium Capryl Amphodiacetate	1.00
Gluconolactone	0.90
Silicone Microemulsion	0.85
Witch Hazel	0.50
PEG-40 Hydrogenated Castor Oil	0.50
Fragrance	0.20
Vitamin E Acetate	0.001
Water	Balance

20

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Example 9

The following formulations are typical of malonate salt stabilized cosmetic sunscreen compositions according to the present invention.

5

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TABLE IX

INGREDIENT	EXAMPLE (WEIGHT %)							
	A	B	C	D	E	F	G	H
Phase A								
Deionized Water	*	*	*	*	*	*	*	*
Carbopol 1382® (2% Active In Water)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Ammonium Malonate	1.0	2.0	5.0	10.0	--	--	--	--
DMAE Malonate	--	--	--	--	1.0	2.0	5.0	10.0
EDTA Disodium	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Butylene Glycol	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67
Glycerin	1.94	1.94	1.94	1.94	1.94	1.94	1.94	1.94
Allantoin	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Phase B								
Amilon® (nylon, silica and lauryl lysine)	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Butyl Octyl Salicylate	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Elefac I-205®	3.00	3.00	3.00	3.00	3.00	3.00	7.00	3.00
Benzophenone-3	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Homosalate	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Octocrylene	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Octyl Methoxycinnamate	7.50	7.50	7.50	7.50	7.50	7.50	7.50	7.50
Octyl Salicylate	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Phenonip	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Tocopheryl Acetate	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Retinyl Linoleate	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Glycerol Monostearate	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Cetyl Alcohol	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
PVP/Eicosene Copolymer	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Amphisol A®	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Parsol 1789®	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Phase C								
Polymethylmethacrylate	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Phase D								
Abil EM 97®	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Polysilicone-11	2.00	6.00	8.00	10.0 0	12.0 0	1.00	4.00	4.00
Cyclomethicone (DC 345)	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Fragrance	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Phase E								
Deionized Water	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83
Potassium Hydroxide (45% solution)	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30
DL-Panthenol	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Phase F								
Actiglide (Special)®	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
Oat Extract	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Ergothioneine	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10

* - to 100

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Example 10

Color stability studies are reported in this Example.

- Testing was conducted with a base formula as outlined under
- 5 Table X. Malonic or glycolic acid in a stated salt form were then incorporated into the base formula resulting in Samples A-D as reported in Table XI

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TABLE X

Base Formula

Surfactant Network	Weight %
Myrj 59 (PEG-100 Stearate)	0.50
Arlacel 60 (Sorbitan Stearate)	1.10
Emulsynt GDL (Glyceryl Dilaurate)	0.50
Cetyl Alcohol	0.50
Cholestrol	0.50
Pristerene 4911 (Stearic Acid)	1.00
Humectant/Emollient	
Glycerin	10.00
Pecosil Pan 418 (Quaternized Panthanol Silicone)	4.00
Clarinol A-80 (Conjugated Linoleic Acid)	1.00
Retinol 15D	0.70
Borage Seed Oil	1.00
Sunscreen	
Parsol 1789 (Avobenzone, UVA)	2.00
Parsol MCX (Octinoxate, UVB)	3.00
Dermoblock OS (Octisalate, UVB)	4.00
Silicone	
Silicone Fluid DC200/10	3.00
Thickener	
Veegum (Mg Al Silicate)	0.60
Keltrol CG1000 (Xanthan Gum)	0.20
Natrosol Plus 330 CS (Cellulose Derivative)	0.50
Aristoflex AVC (Taurate/VP Copolymer)	0.40
Powder	
Titanium Dioxide (50% in solvent)	3.00
Ganspearl GMP 0820 (PMMA)	1.20
Preservative/Anti-Oxidant etc.	
Methylparaben	0.30
Propylparaben	0.20
Phenoxyethanol	0.40
Glycosil	0.10
Disodium EDTA	0.10
BHT	0.20
Dequest 2006	0.53
Deionised water	to 100

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TABLE XI

Full Formula

Formula	Acid	Base
A	4% Glycolic Acid	3.6% DMAE
B	4% Glycolic Acid	0.8% Ammonia
C	2.5% Malonic Acid	3.2% DMAE 0.5% Tris Amino
D	2.5% Malonic Acid	0.7% Ammonia

*DMAE = Dimethylaminoethanol

5 ** Tris Amino = Tri(hydroxymethyl)amino methane

- The full formulas were filled in glass jars and placed under various conditions for evaluation in a Color Stability Test.
- 10 Test conditions included ovens kept at 22°C, 37°C, 40°C, 50°C and 60°, for evaluating thermal stability. The test conditions also included stations wherein the formulas were exposed to natural (northern) light and fluorescent light at room temperature, to evaluate light stability.
- 15 The samples were kept in ovens or exposed to light for two weeks. Samples were then evaluated for changes in color. A color chart was utilized with color grade ranging from 1 (white) to 20 (bright yellow). When the color grade increased from 1 to 20, this reflected change towards
- 20 yellow.

Stability results are reported in Table XII. These results show that formulas C and D (malonate) were more effective at controlling color body formation occurring through thermal stress than formulas A and B (glycolates). Malonates were

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also more effective than glycolates in stabilizing against natural (northern) and fluorescent light degradation.

TABLE XII

5 Stability Results

Formula	Acid	Base	22°C	37°C	43°C	50°C	60°C	North Light	Fluor Light
A	4% Glycolic Acid	3.6% DMAE	12	14	15	15	16	9	9
B	4% Glycolic Acid	2.9% Ammonia	14	14	16	16	15	17	17
C	2.5% Malonic Acid	3.2% DMAE 0.5% Tris Amino	10	10	9	9	9	11	10
D	2.5% Malonic Acid	2.5% Ammonia	10	10	10	12	11	10	11

The foregoing description and examples illustrate selected
10 embodiments of the present invention. In light thereof various and modifications will be suggested to one skilled in the art, all of which are within the spirit and purview of this invention.

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CLAIMS

1. A cosmetic composition comprising:
 - (i) from about 0.0001% to about 30% by weight of a salt of malonic acid;
 - 5 (ii) from about 0.05% to about 40% by weight of an organic sunscreen agent having a chromophoric group active within the ultraviolet radiation range of 280 to 400 nm; and
 - (iii) from about 1% to about 99.9% by weight of a
10 cosmetically acceptable carrier.
2. The composition according to claim 1 wherein the malonic acid is present as a half neutralized and a fully neutralized acid in a molar ratio ranging from about 1000:1 to about 1:1000, respectively.
15
3. The composition according to claim 2 wherein the molar ratio is about 2:1 to about 1:200.
4. The composition according to any of the preceding claims wherein the salt has a cationic counterion to malonate
20 which is an inorganic cation selected from lithium, sodium, potassium, magnesium, calcium, ammonium and combinations thereof.
5. The composition according to any of the preceding claims wherein the salt has a cationic counterion to malonate
25 which is an organic cation having from 2 to 1,000 carbon atoms selected from polyethyleneimine, triethanolamine, diethanolamine, propanolamine, monoethanolamine,

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methyllamine, ethyllamine, propyllamine, isopropyllamine,
butyllamine, isobutyllamine, t-butyllamine, pentyllamine,
isopentyllamine, hexyllamine, cyclohexyllamine,
cyclopentyllamine, norbornyllamine, octyllamine,
5 ethyllhexyllamine, nonyllamine, decyllamine, pyrrolidone,
amino acids, 2-amino-2-methyl-1-propanol,
dimethylethanolamine, tris(hydroxymethyl)amino methane
and combinations thereof.

6. The composition according to any of the preceding claims
10 wherein the sunscreen agent is 4,4'-t-butyl-
methoxydibenzoylmethane.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, EMBASE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Grillenberger, S

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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